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Analysis of isotopes of radium, uranium and thorium 210Pb-210Po

Roos, Per

Publication date:
2009

Document Version
Publisher's PDF, also known as Version of record

Analysis of isotopes of radium, uranium and thorium. ^{210}Pb-^{210}Po

Per Roos

Risø National Laboratory for Sustainable Energy, Technical university of Denmark

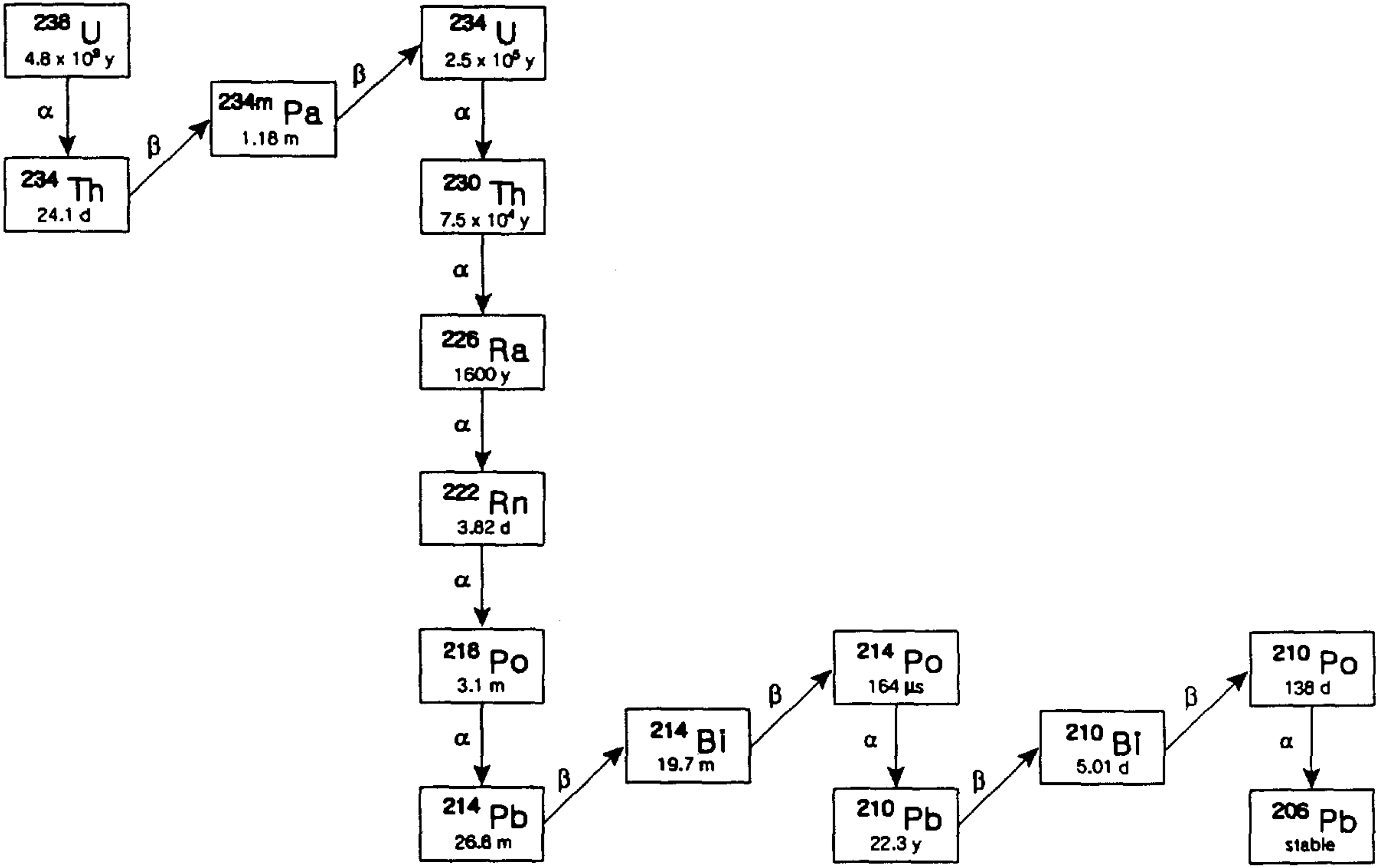


Figure 1. Uranium series (4n + 2 series)

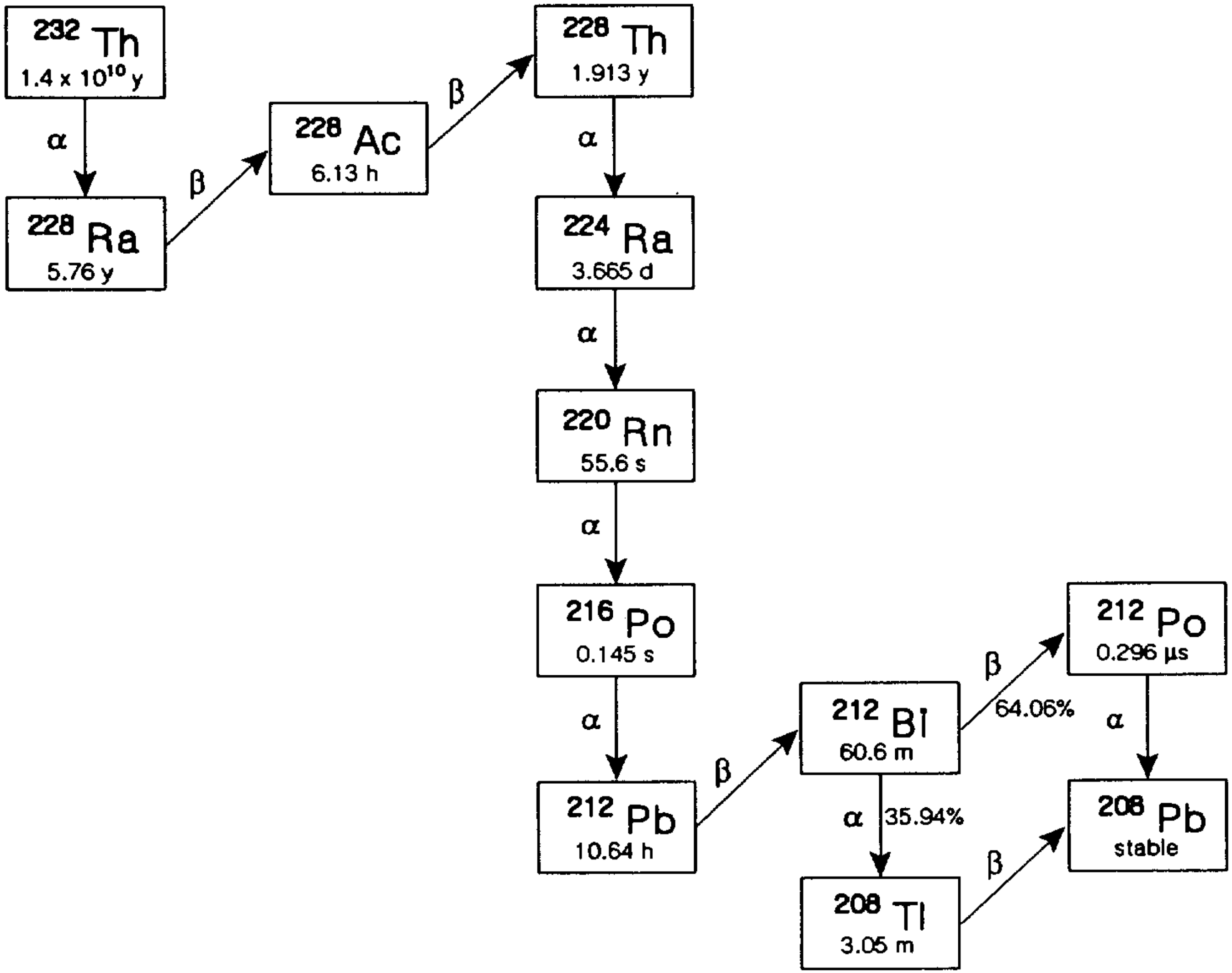


Figure 2. Thorium series (4n series)

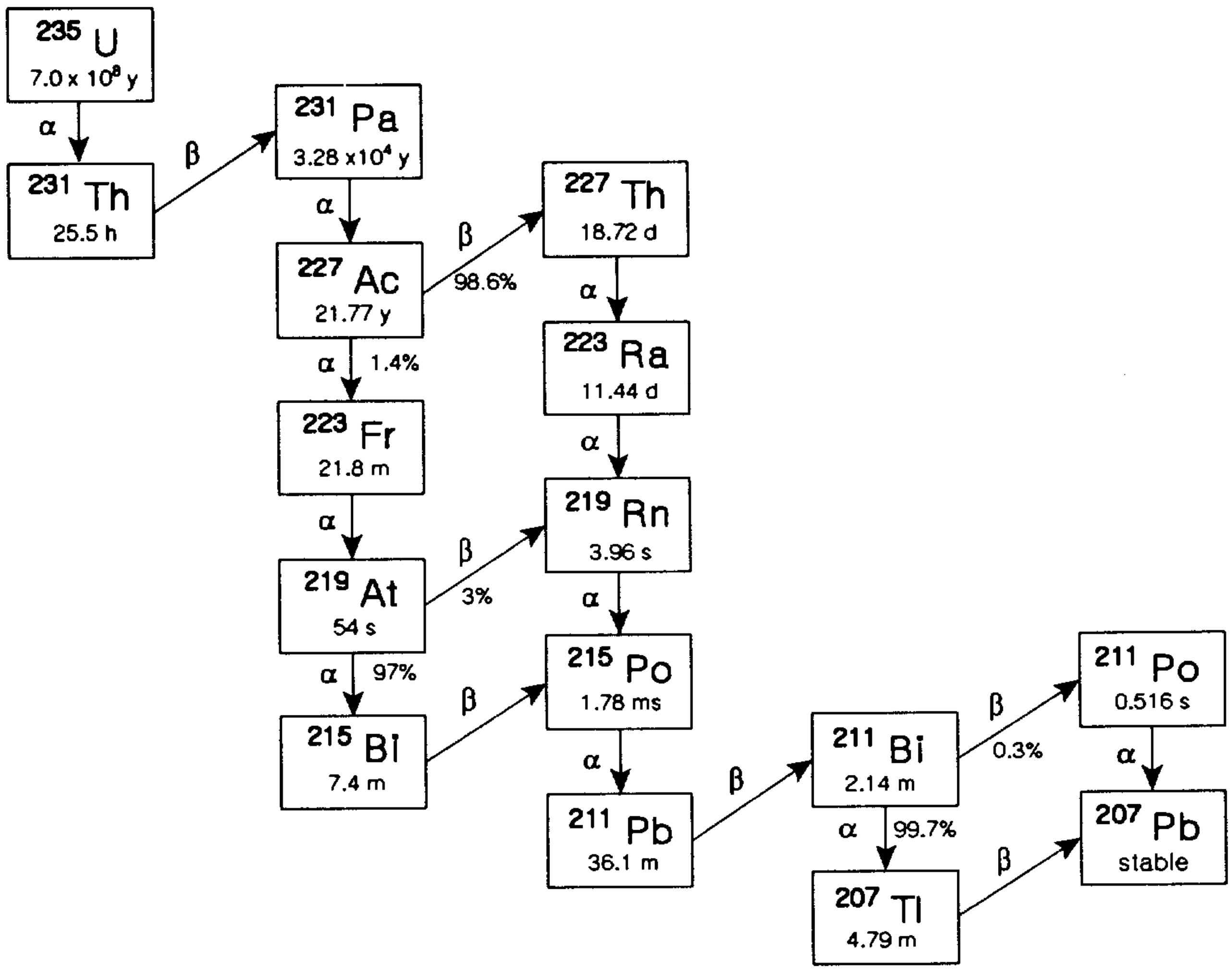


Figure 3. Actinium series (4n + 3 series)

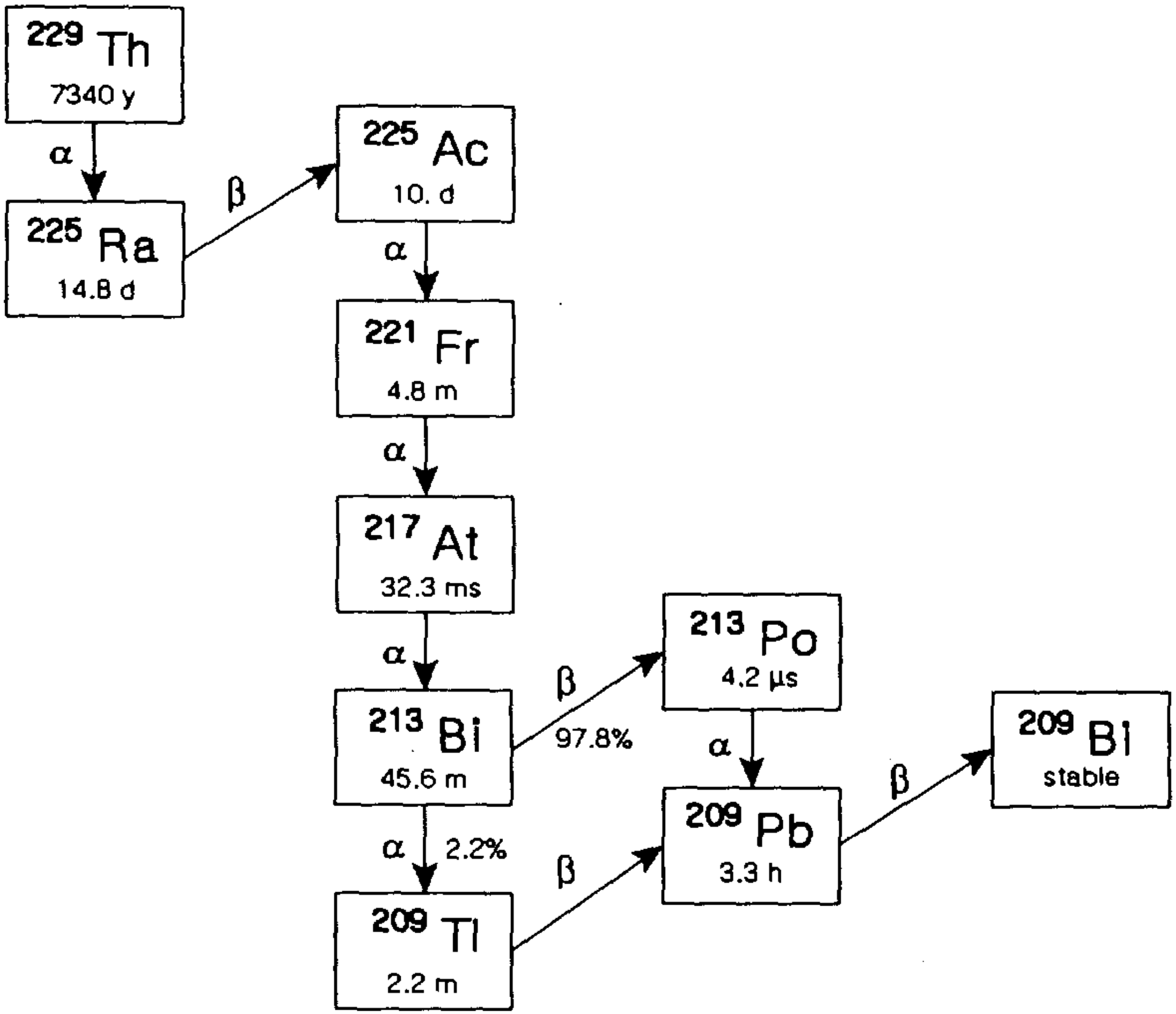


Figure 4. 4n + 1 series

Radium isotopes

$$^{230}\mathrm{Th} \xrightarrow{\alpha:\ 7.54\times10^{4}\ \mathrm{a}} {}^{226}\mathrm{Ra} \xrightarrow{\alpha:\ 1.60\times10^{3}\ \mathrm{a}} {}^{222}\mathrm{Rn} \xrightarrow{\alpha:\ 3.82\ \mathrm{d}} {}^{218}\mathrm{Po} + \mathrm{daughters}$$

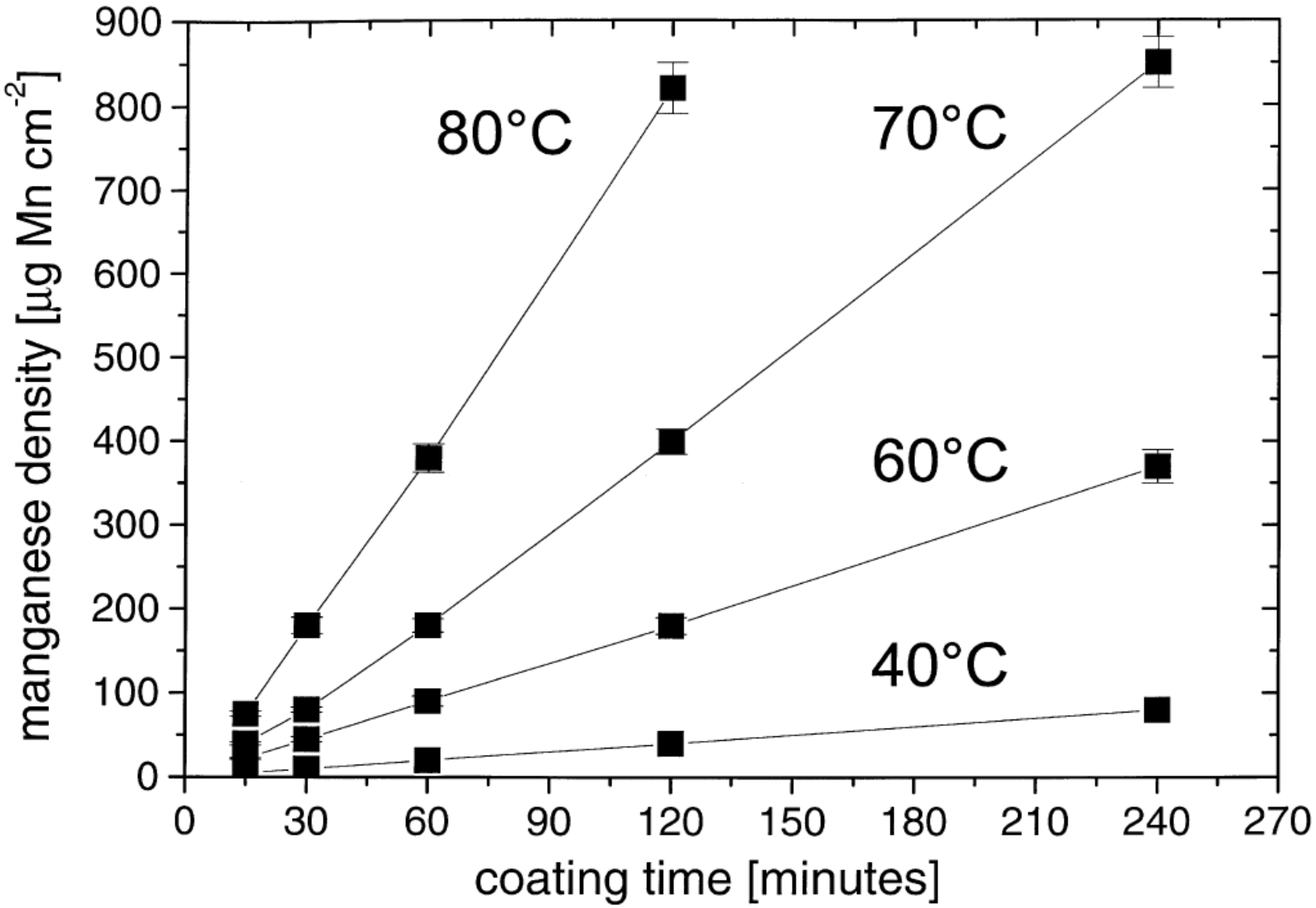
$$^{232}\mathrm{Th} \xrightarrow{\alpha:\ 1.40\times10^{10}\ \mathrm{a}} {}^{228}\mathrm{Ra} \xrightarrow{\beta:\ 5.76\times10^{0}\ \mathrm{a}} {}^{228}\mathrm{Ac} \xrightarrow{\beta:\ 6.13\ \mathrm{h}} {}^{228}\mathrm{Th} + \mathrm{daughters}$$

$$^{228}\mathrm{Th} \xrightarrow{\alpha:\ 1.91\times10^{0}\ \mathrm{a}} {}^{224}\mathrm{Ra} \xrightarrow{\beta:\ 3.66\ \mathrm{d}} {}^{220}\mathrm{Rn} \xrightarrow{\alpha:\ 55.6\ \mathrm{d}} {}^{216}\mathrm{Po} + \mathrm{daughters}$$

$$^{227}\mathrm{Th} \xrightarrow{\alpha:\ 18.72\ \mathrm{d}} {}^{223}\mathrm{Ra} \xrightarrow{\alpha:\ 11.43\ \mathrm{d}} {}^{219}\mathrm{Rn} \xrightarrow{\alpha:3.96\ \mathrm{s}} {}^{215}\mathrm{Po} + \mathrm{daughters}$$

Adsorption of Ra on MnO_2 & direct alpha spectrometry

Coating of polyamid (Nylon) with MnO_2 ($KMnO_4$ solution)



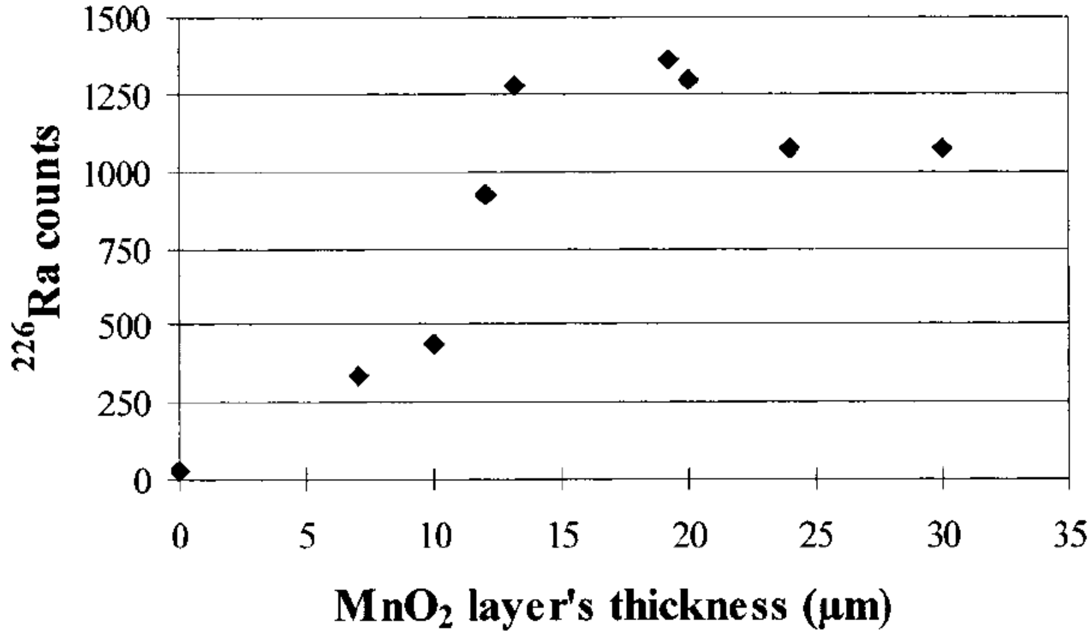


Figure 2. ^{226}Ra adsorption versus MnO_2 layer thickness.

Table 1. Data from the Preparation of the MnO_2 Layer at Different Temperatures

prepn temp (°C)	MnO_2 layer thickness (μm)	fwhm (keV)	^{133}Ba rec (%)	^{226}Ra counts in α-spectrum
50	14	61.5	88	2576 ± 52
60	15	78.3	100	2569 ± 51
65	16	87.0	100	2657 ± 50
70	18	109.7	100	2586 ± 52
80	23	130.2	100	2675 ± 54

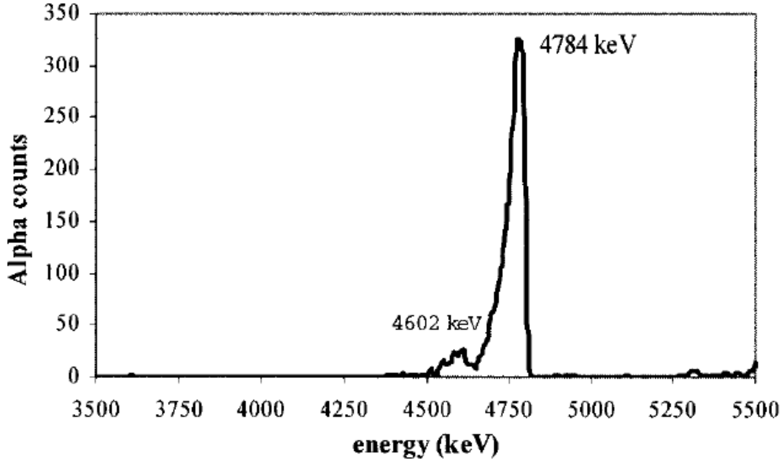


Figure 4. α-Spectrum obtained from a MnO_2 disk prepared at 50 °C. The emission percentages are 95 and 5% for 4784 and 4602 keV, respectively.

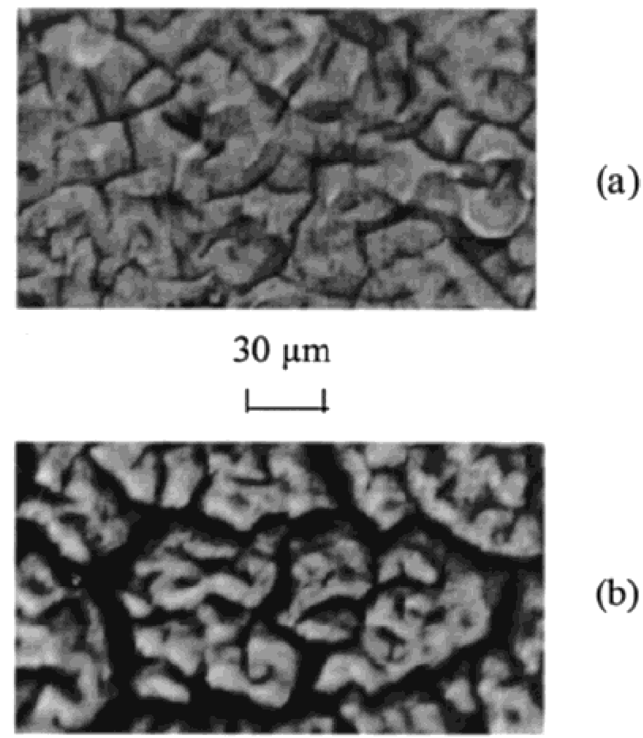


Figure 3. Pictures of MnO_2 deposit on polyamide-6,6 with a 20× enlargement: (a) thickness of 15 μm and (b) thickness of 23 μm.

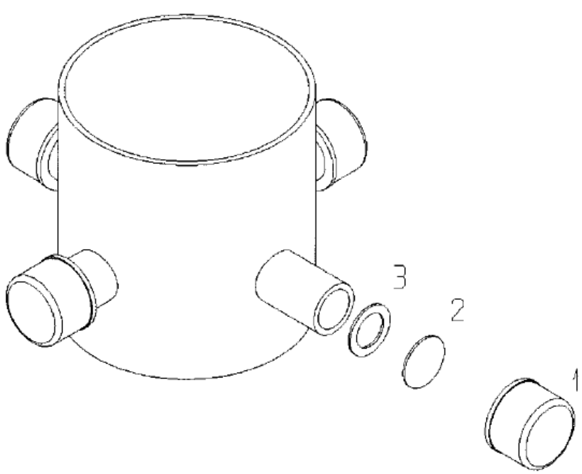


Figure 1. Reactor for the preparation of the MnO_2 disks: 1, Bakelite top; 2, 6,6PA disk; 3, rubber gasket.

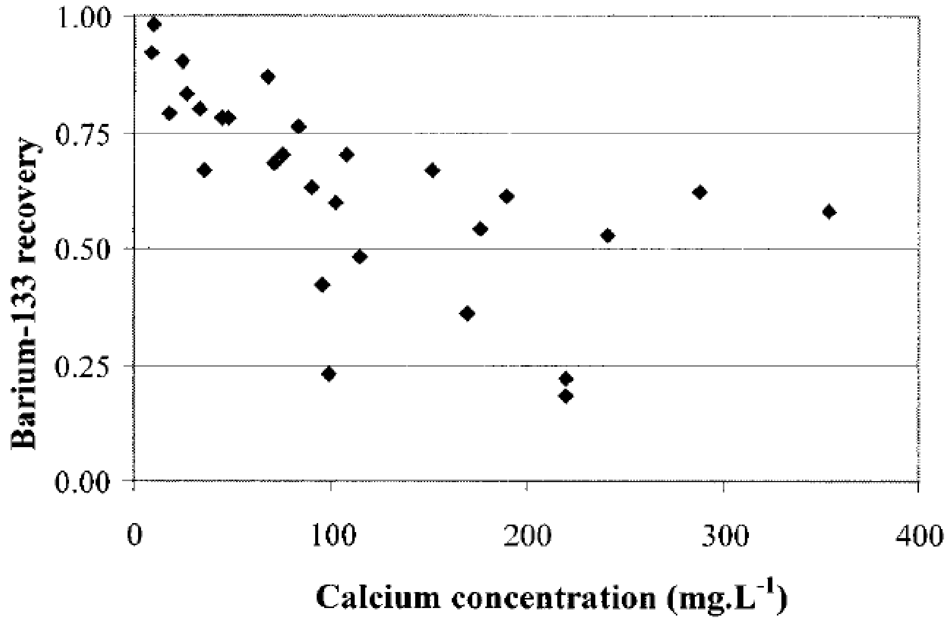
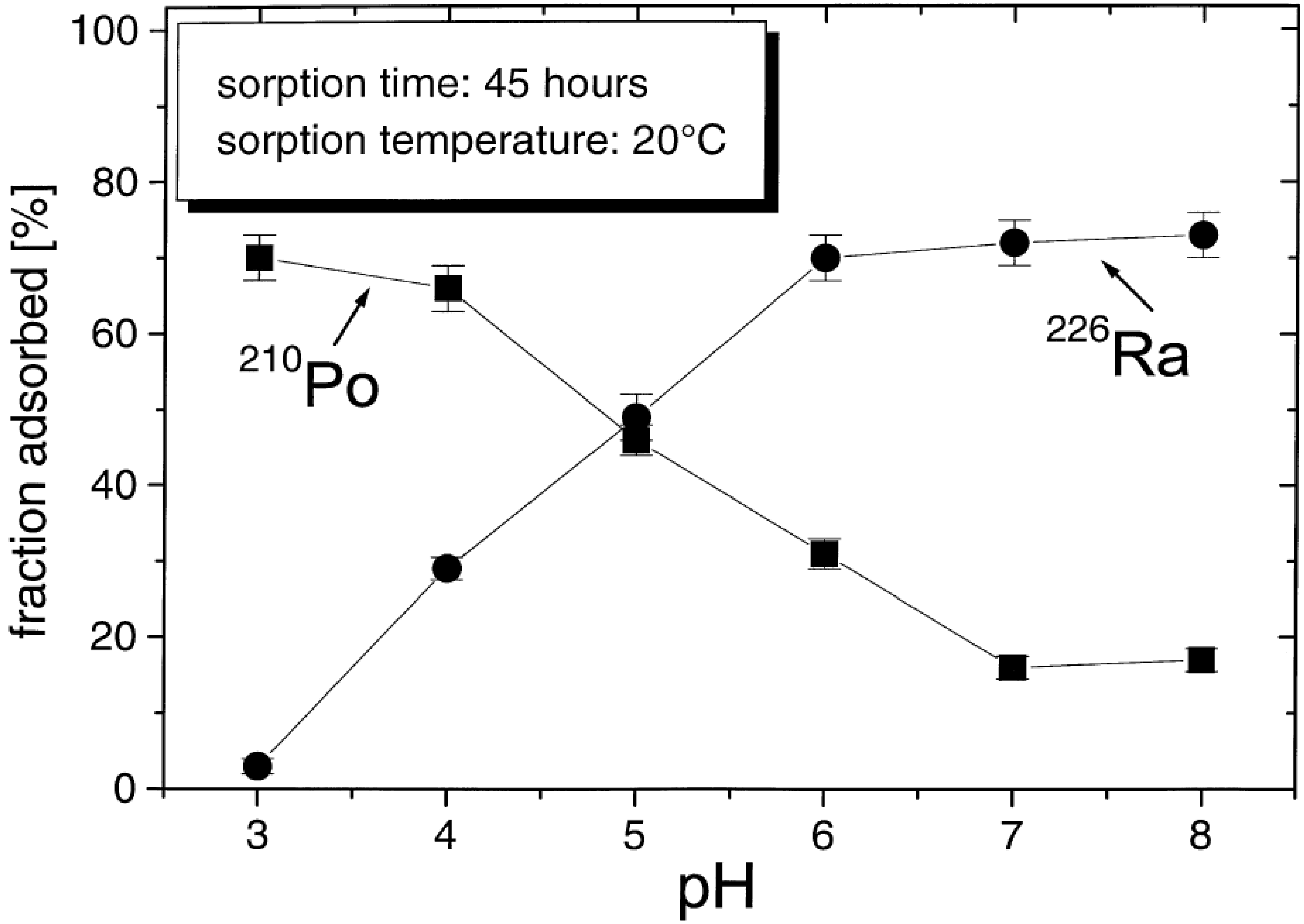
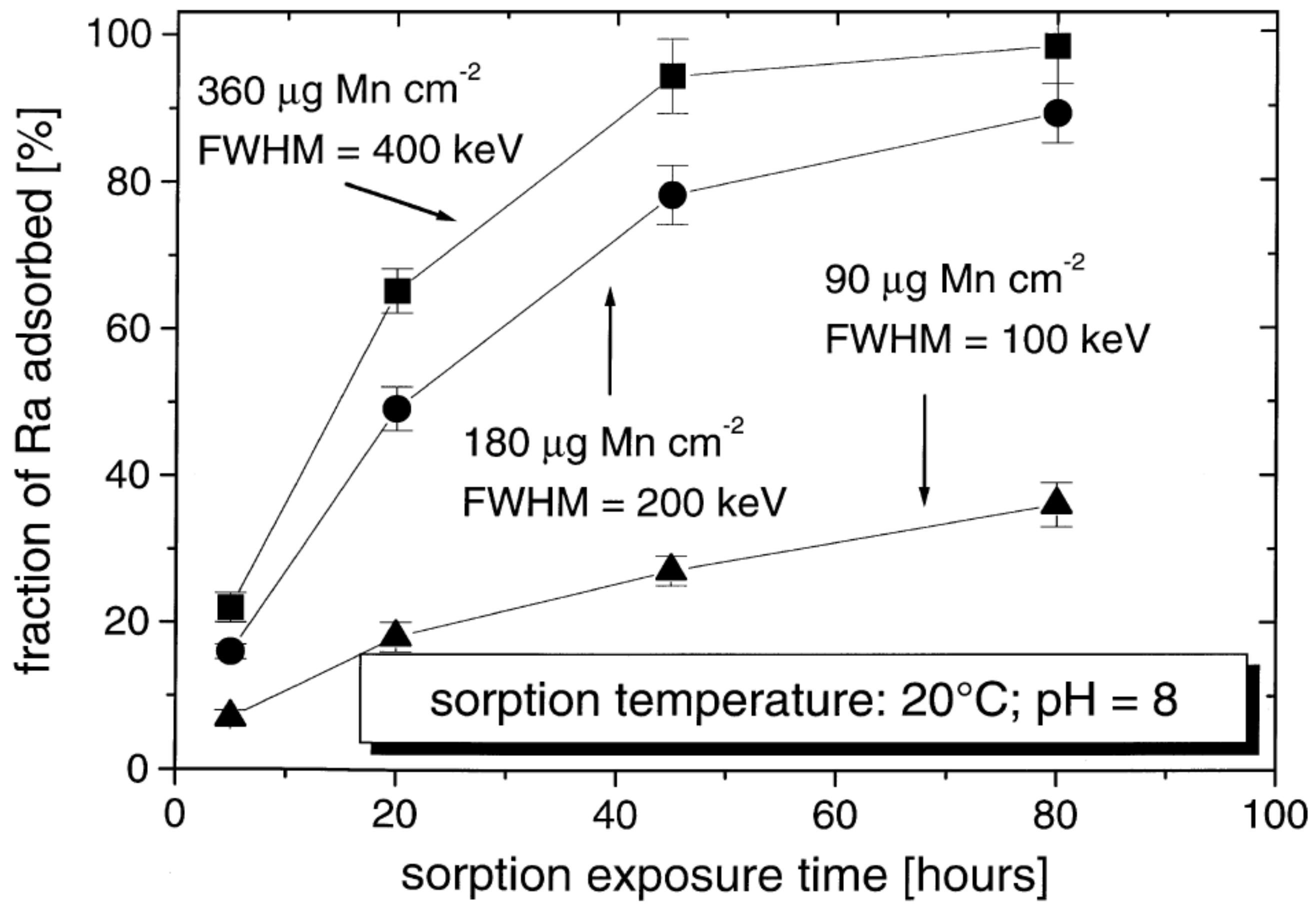


Figure 8. Calcium concentration of mineral waters versus the ^{133}Ba recovery.



$$2S(OH)^{-} + Ra^{2+} \leftrightarrow (SOH)_2Ra,$$

$$2S(H)^{+} + PoO_3^{2-} \leftrightarrow (SO)_2Po + H_2O.$$



……half-life of Ra-224 is 88h

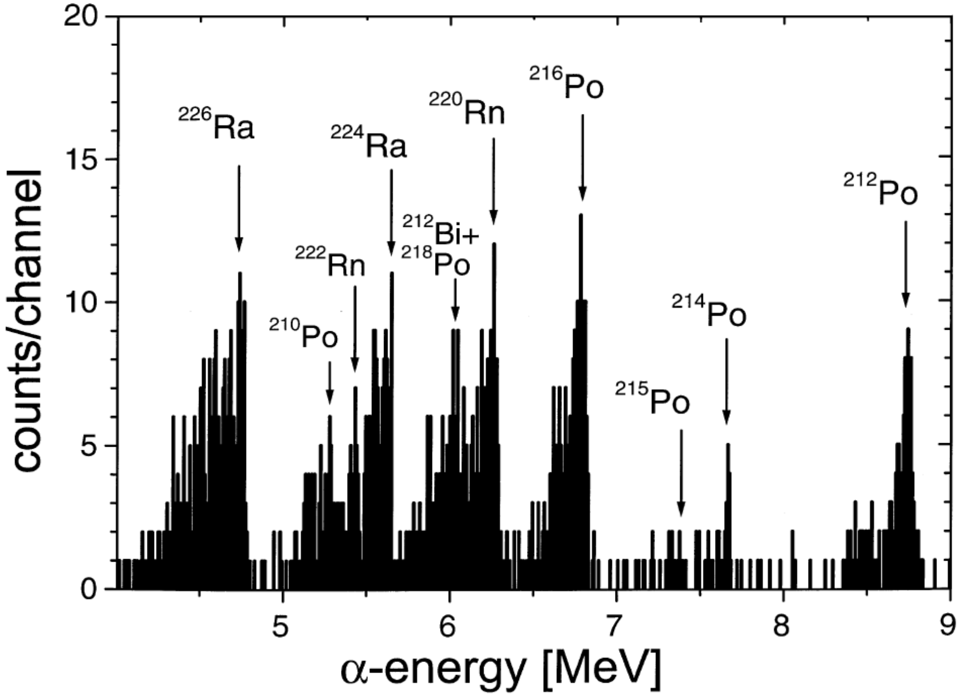
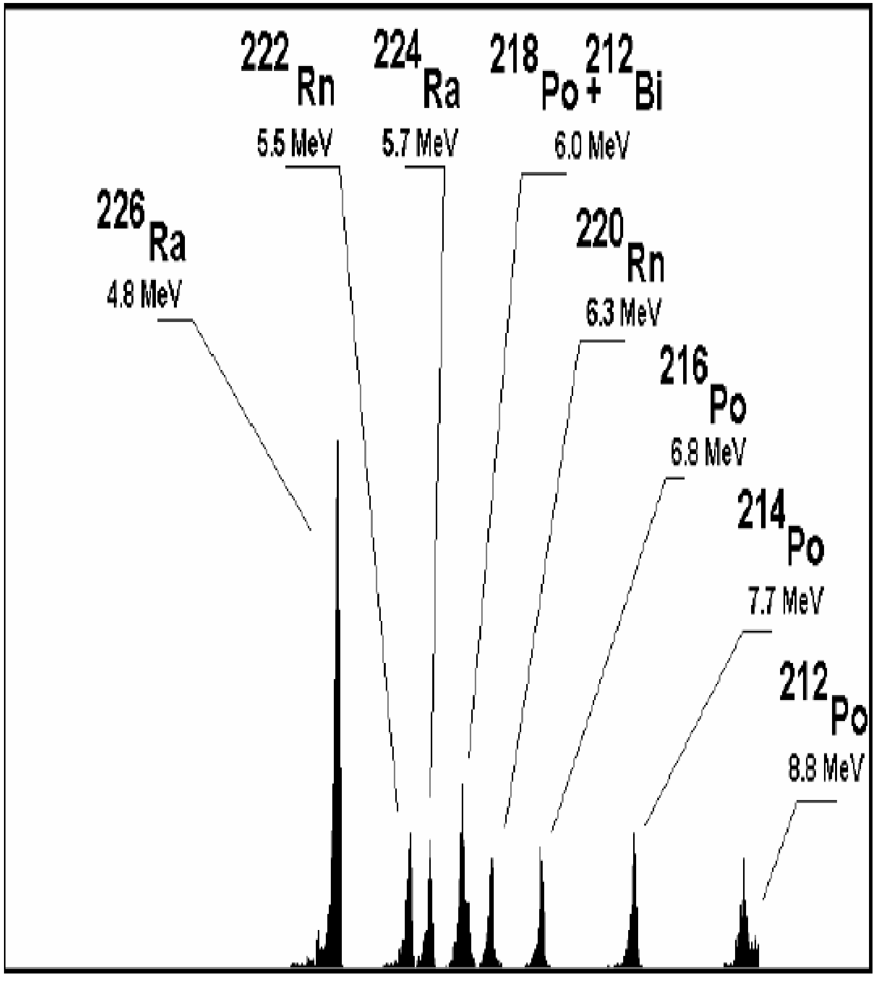


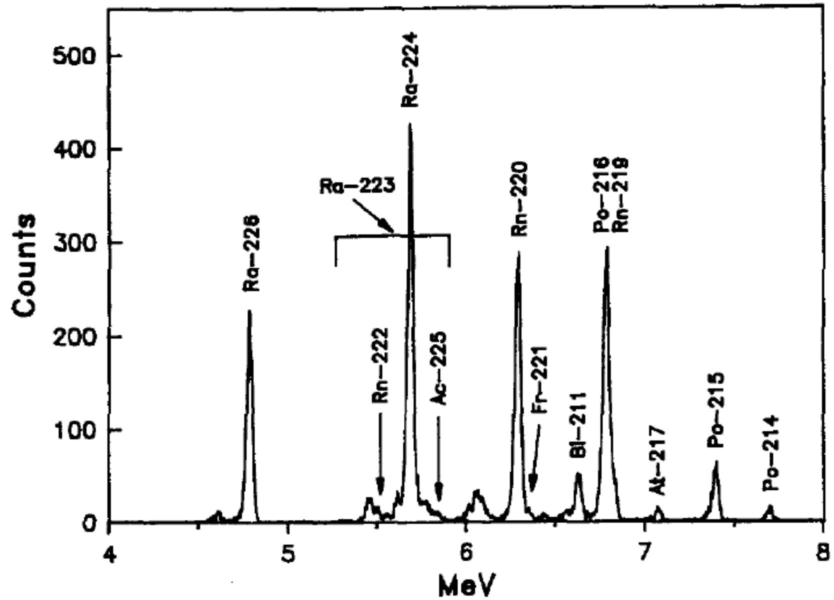
Fig. 4. Typical α-spectrum of ^{226}Ra and ^{224}Ra (including short-lived proxies) obtained from water sample G-1 on a disc coated with a manganese density of 180 μg cm^{-2}.

Very thin MnO2 layer, poor yield but excellent resolution

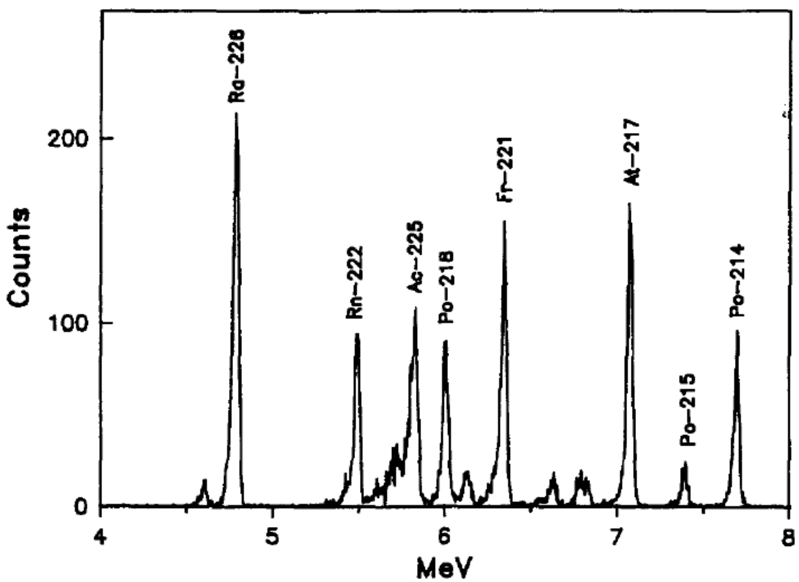


Electrodeposited sources

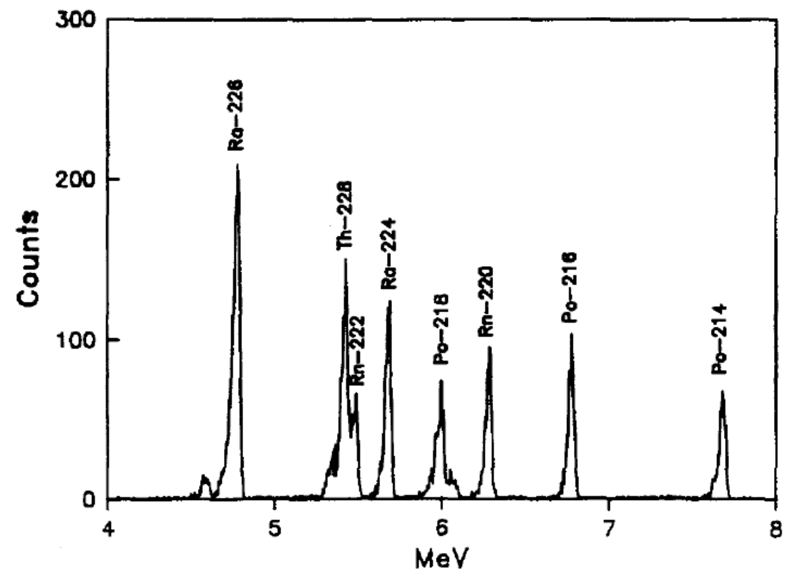
Direct



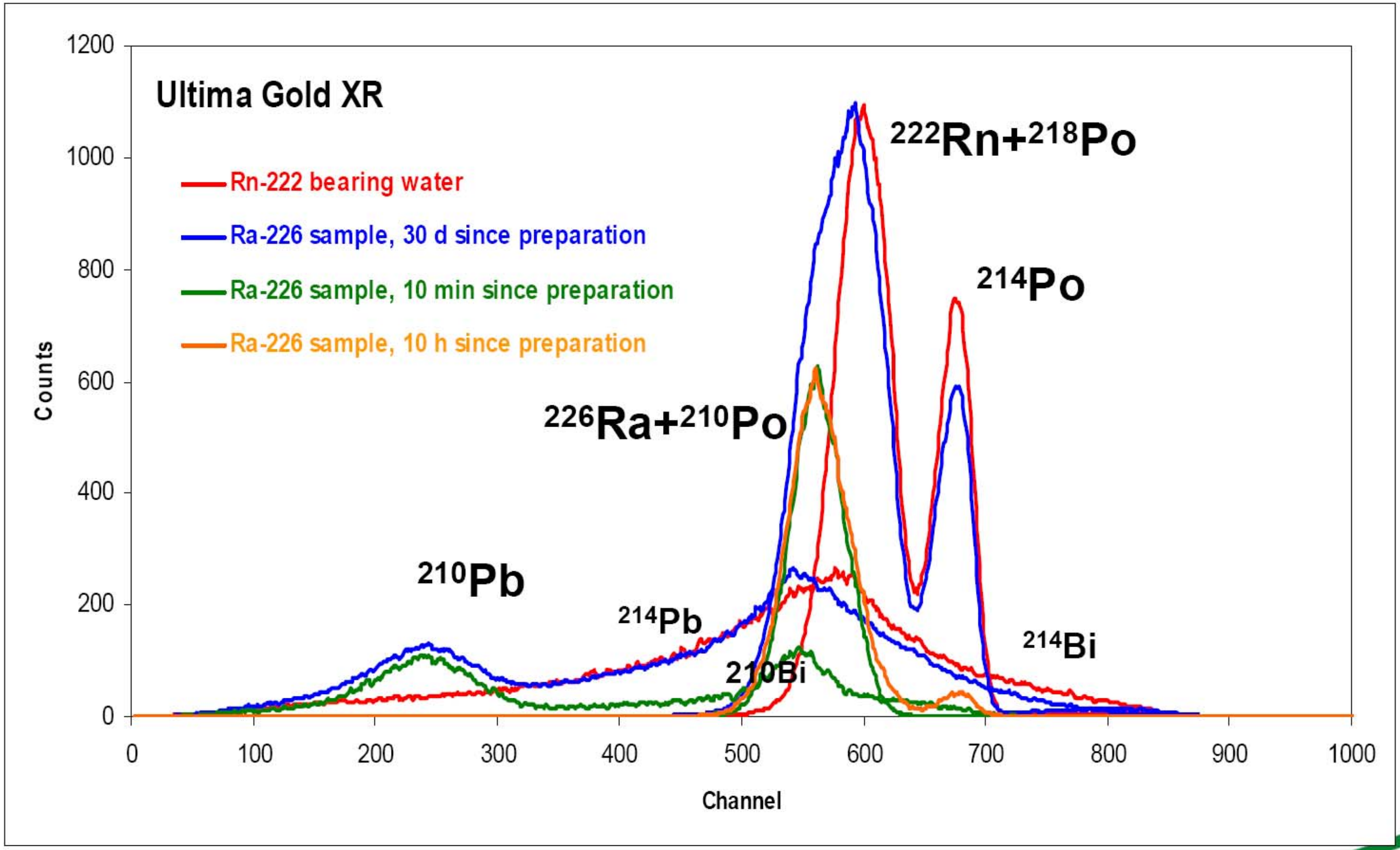
20 days



6 months

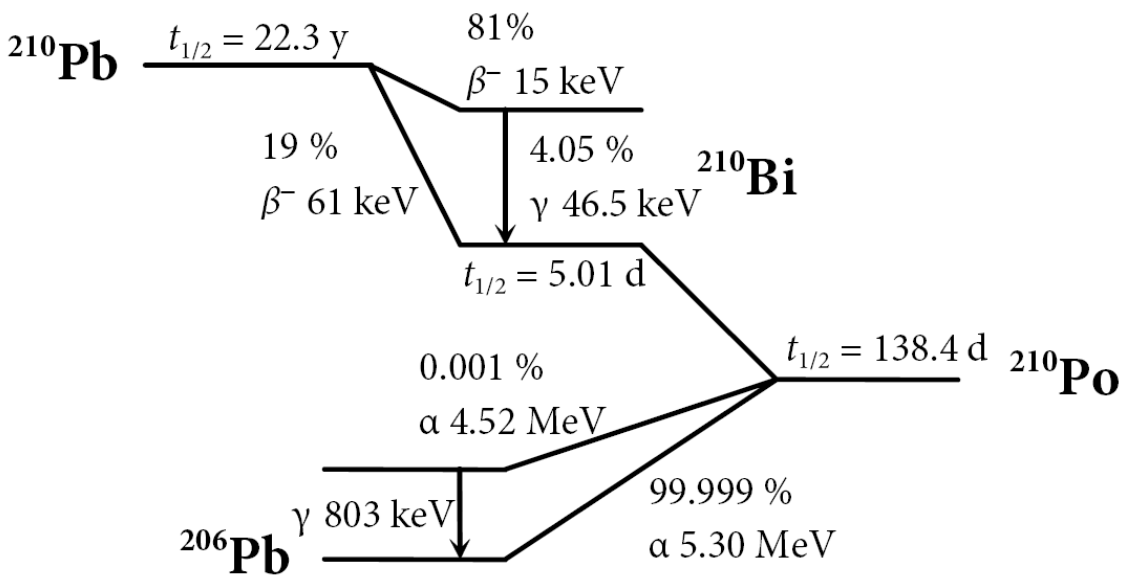


The α and β spectra of the homogenous samples prepared from ^{222}Rn-bearing water and ^{226}Ra standard.

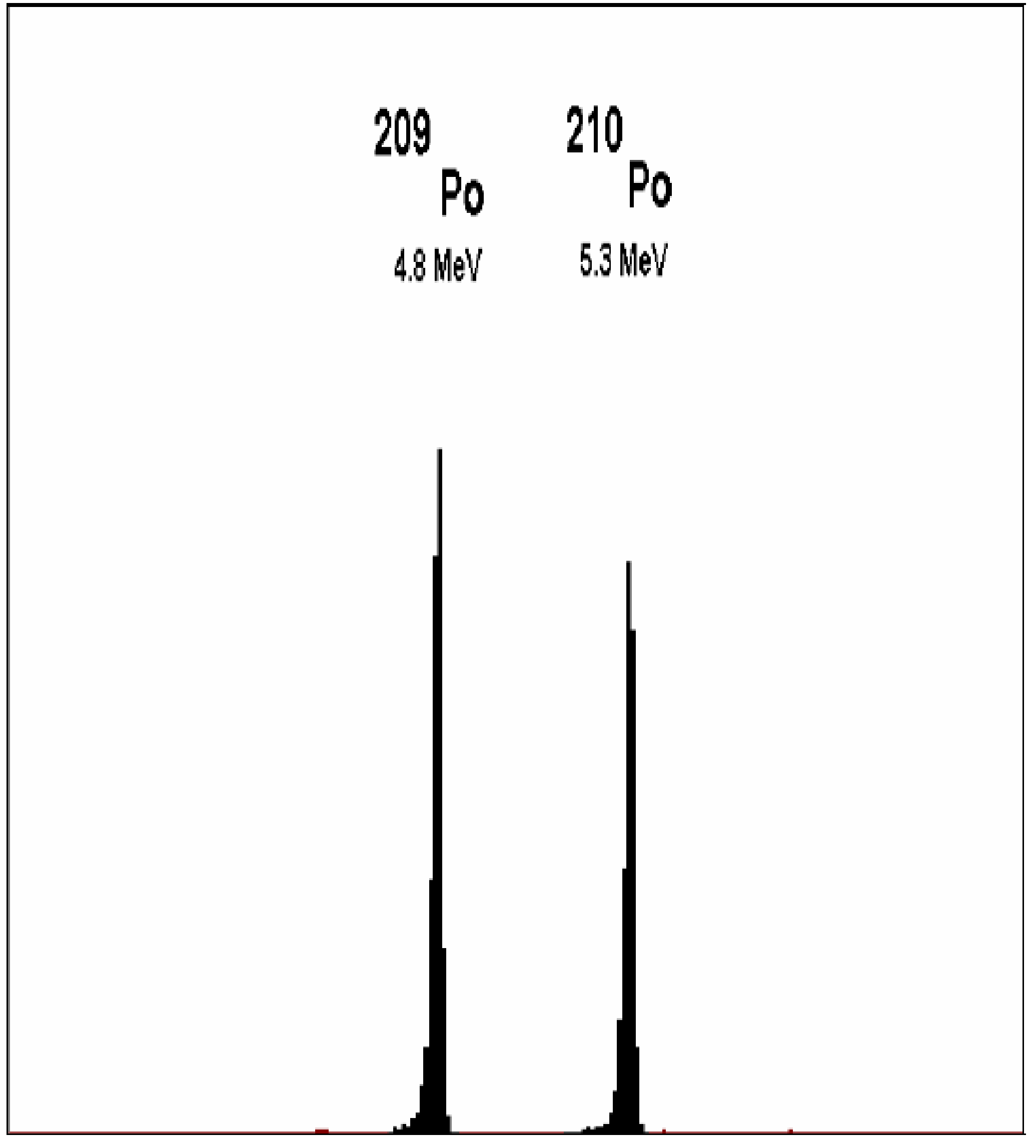


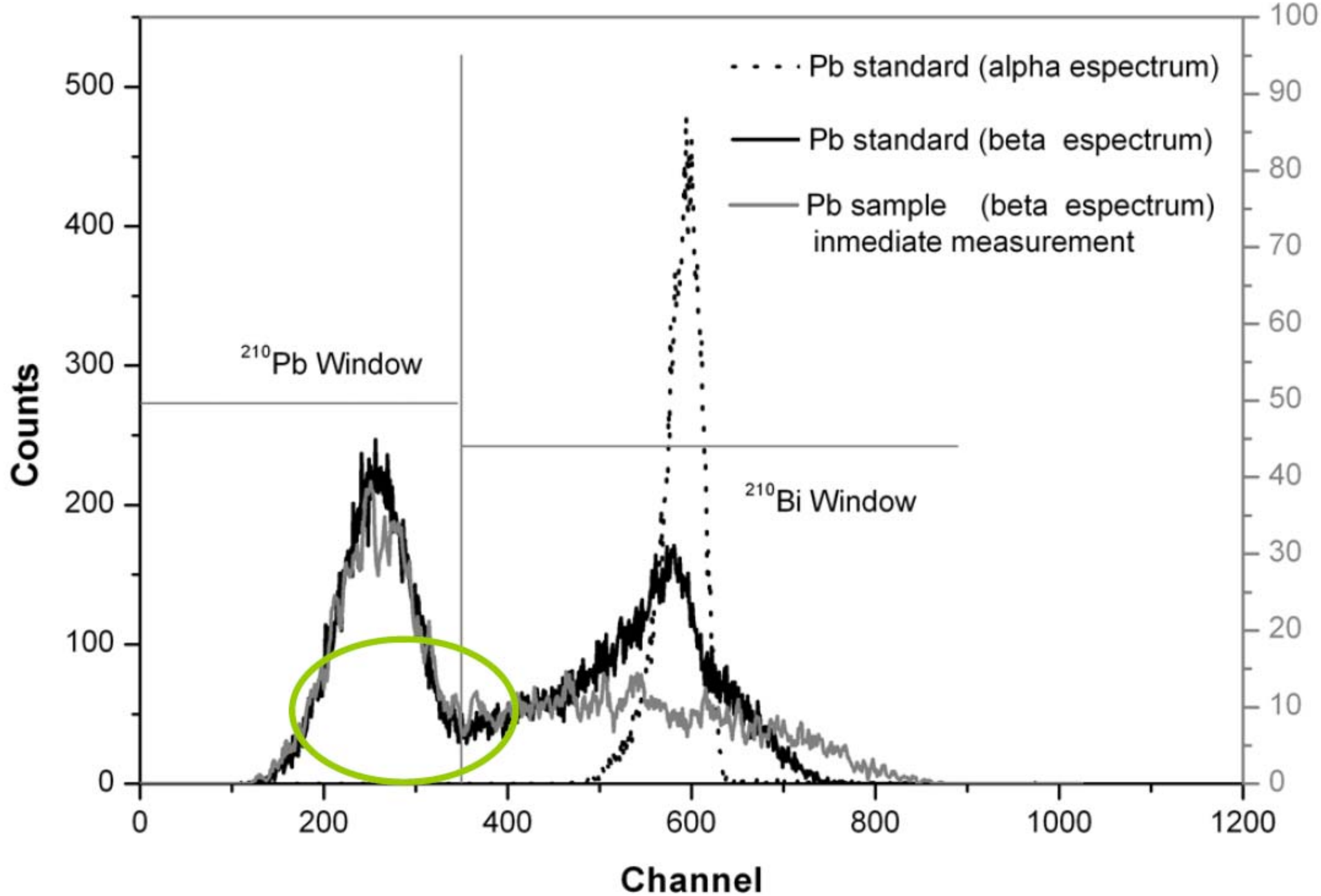
Analysis of ^{226}Ra in water

- **Weigh up a suitable amount of water (10 litre is mostly sufficient).**
- **Add HNO_3 to pH 1-2.**
- **Add ^{133}Ba tracer (ca 10 Bq).**
- **Add about 13 ml of a 0.2M $KMnO_4$.**
- **Adjust pH to about 8-9 with ammonia.**
- **Add 15 ml 0.3M $MnCl_2$ and stir for some 5 minutes.**
- **Adjust with $KMnO_4$ or $MnCl_2$ to make the sample water phase slightly pink.**
- **Collect the precipitate and centrifuge**
- **Dissolve precipitate in 1M HCl-1%H_2O_2.**
- **Add about 2g K_2SO_4+1ml H_2SO_4 and dilute to 100 ml with water.**
- **Heat the sample to dissolve the K_2SO_4 completely.**
- **Add 30 mg Pb^{2+}. Heat for 20 minutes and stir.**
- **Centrifuge the precipitate and discard supernate.**
- **Wash precipitate with 100 ml of a solution of 0.2M H_2SO_4 and 0.1 M K_2SO_4**
- **Centrifuge the precipitate and discard supernate**
- **Dissolve the $PbSO_4$-precipitate with 3ml 0.1M EDTA at pH 10.**
- **Transfer the solution to the scintillation vial (low diffusion PE-vial).**
- **Wash centrifuge tube with 2 ml 0.1M EDTA and transfer to Scintillation vial.**
- **Add 10ml OptiFluor 0 and fill with deionised water to total 20 ml.**
- **Allow for ingrowth of ^{222}Rn during 3 weeks and measure by LSQ.**



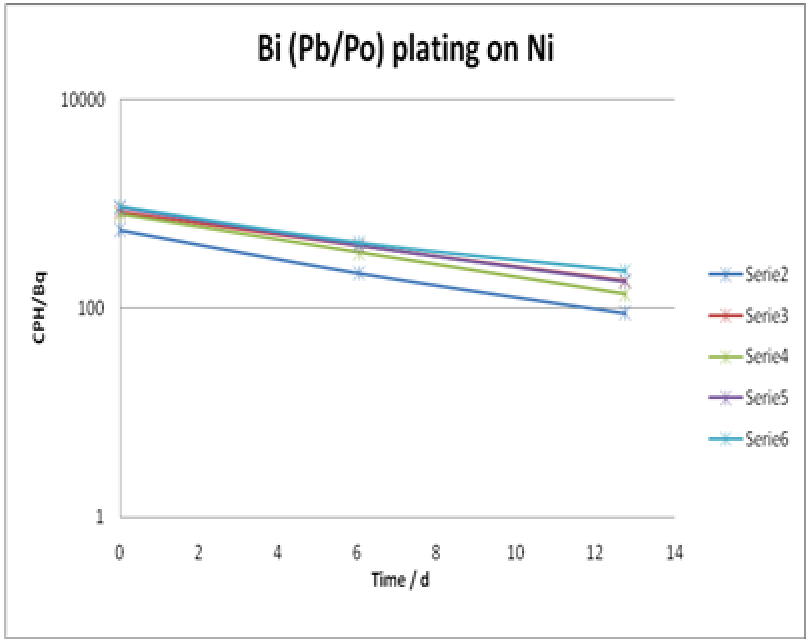
^{210}Pb
$t_{1/2}$ = 22.3 y
81%
β^- 15 keV
19 %
β^- 61 keV
4.05 %
γ 46.5 keV
^{210}Bi
$t_{1/2}$ = 5.01 d
$t_{1/2}$ = 138.4 d
^{210}Po
0.001 %
α 4.52 MeV
γ 803 keV
^{206}Pb
99.999 %
α 5.30 MeV


209 Po
4.8 MeV
210 Po
5.3 MeV


Pb standard (alpha espectrum)
Pb standard (beta espectrum)
Pb sample (beta espectrum)
inmediate measurement
^{210}Pb Window
^{210}Bi Window
Counts
Channel
0
100
200
300
400
500
0
200
400
600
800
1000
1200
0
10
20
30
40
50
60
70
80
90
100

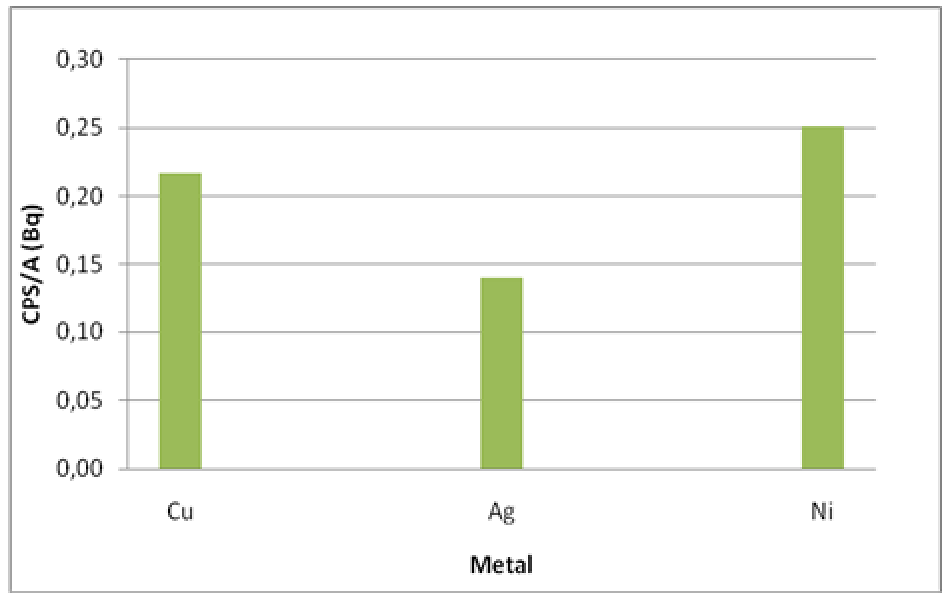
Losses of polonium when wet ashing

Sample matrix	Loss %
Birch (*Betula pendula*) leaves	16.5
Lichen (*Cladonia alpestris*)	24.5
Peat	24.5
Algae (*Fucus serratus*)	55.8
Peat	23.4
Plaice (*Platichthys flesus*)	30.3
Algae (*Fucus vesiculosus*)	32.0
Algae (*Fucus vesiculosus*)	38.3
AVERAGE	**30.7+/-11.4**



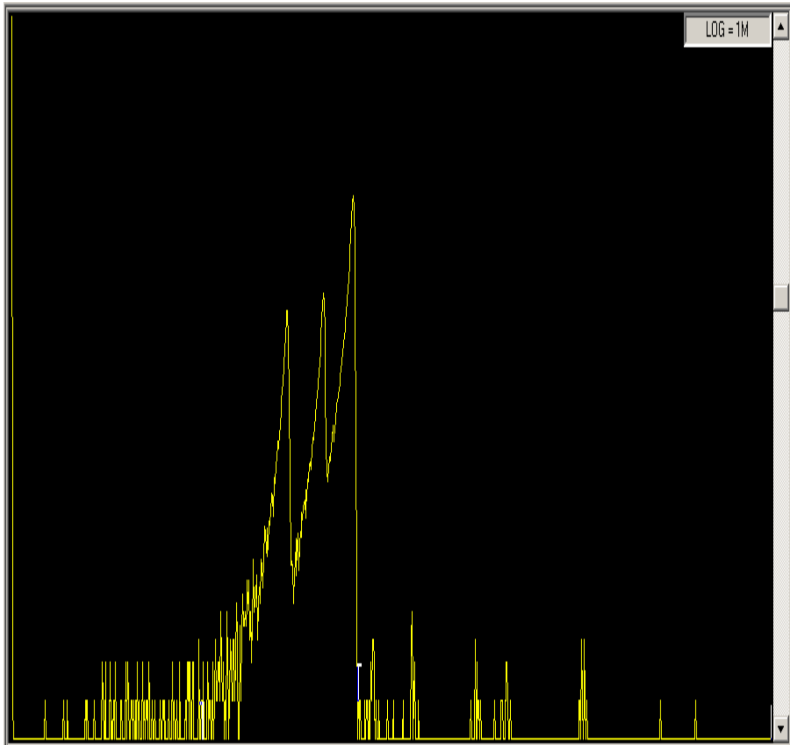
Bi (Pb/Po) plating on Ni
10000
100
1
CPH/Bq
0
2
4
6
8
10
12
14
Time / d
Serie2
Serie3
Serie4
Serie5
Serie6

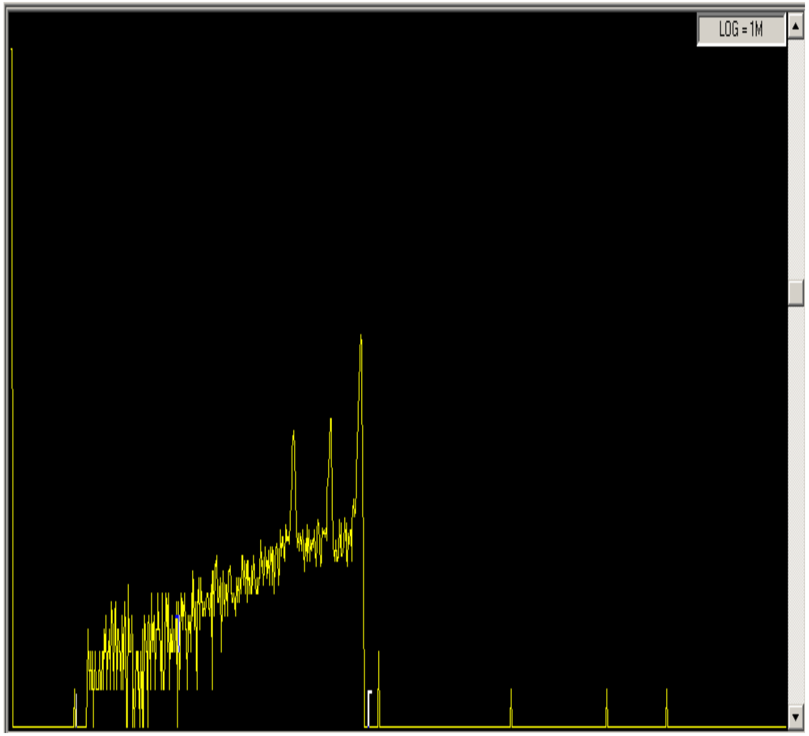
Pb plating



0,30
0,25
0,20
0,15
0,10
0,05
0,00
CPS/A (Bq)
Cu
Ag
Ni
Metal

…heating the Ag-disc





More studies on losses when heating….

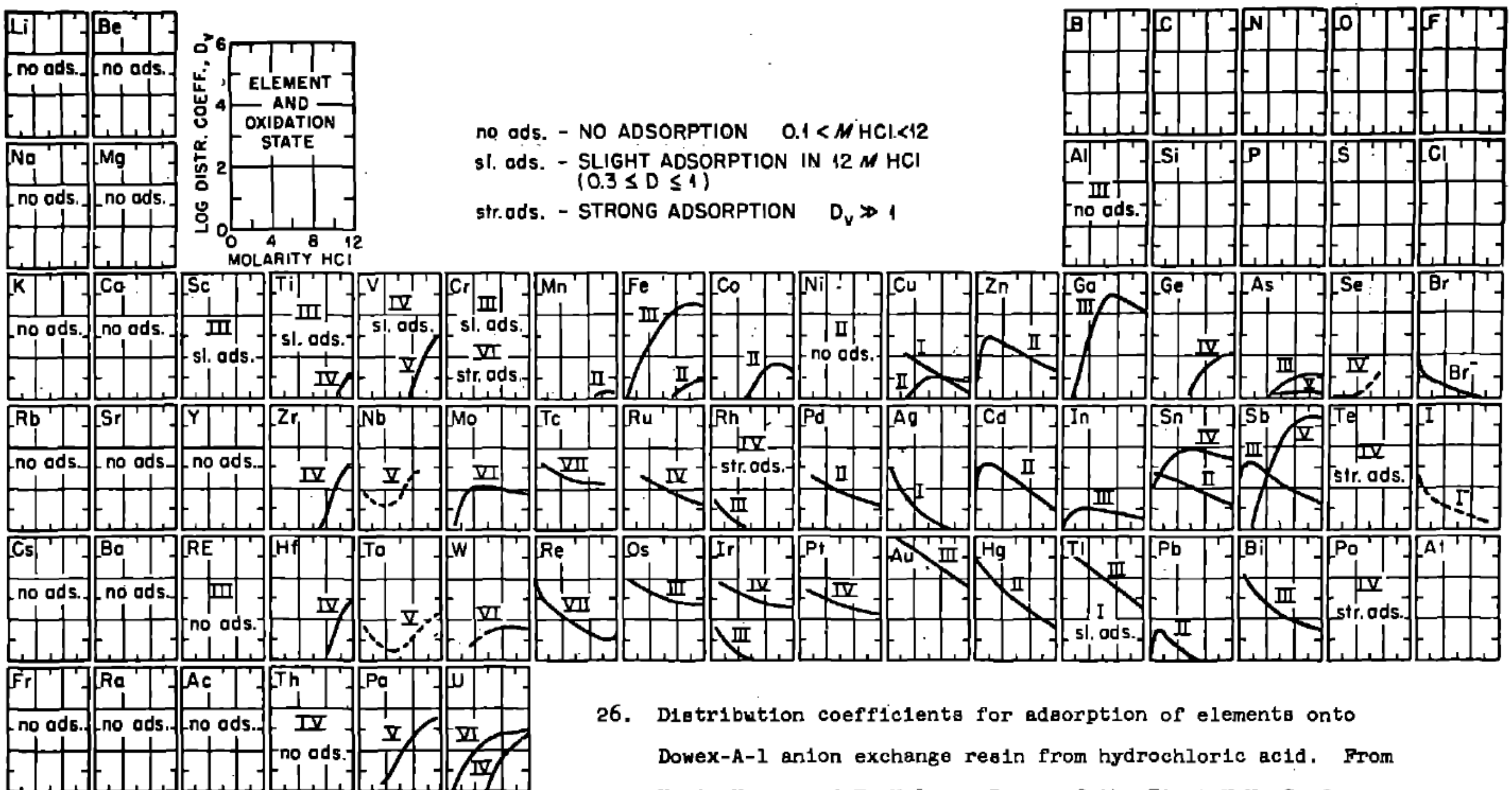
Tab. 32: Reproducibility of spontaneous depositions and activity loss by heating experiments. Added Po-208 activity was in all experiments 90 mBq. Deposition time for nickel was 5 h and for silver 18 h. Average values are shown in bold. The discs were heated 30 min on a hotplate at > 300 °C.

Nickel yield (%)	Yield after heating	Loss (%)	Silver yield (%)	Yield after heating	Loss (%)
70	44	37	102	101	2
47	30	36	104	102	2
43	35	19	98	87	11
77	49	37	98	93	5
86	53	38	104	96	8
48	33	31	103	102	1
41	28	31	105	98	6
71	64	10	99	97	2
42	33	22	102	93	10
85	62	27	76	73	4
61 ± 18	**43 ± 13**	**29 ± 9**	**99 ± 9**	**94 ± 9**	**5 ± 4**

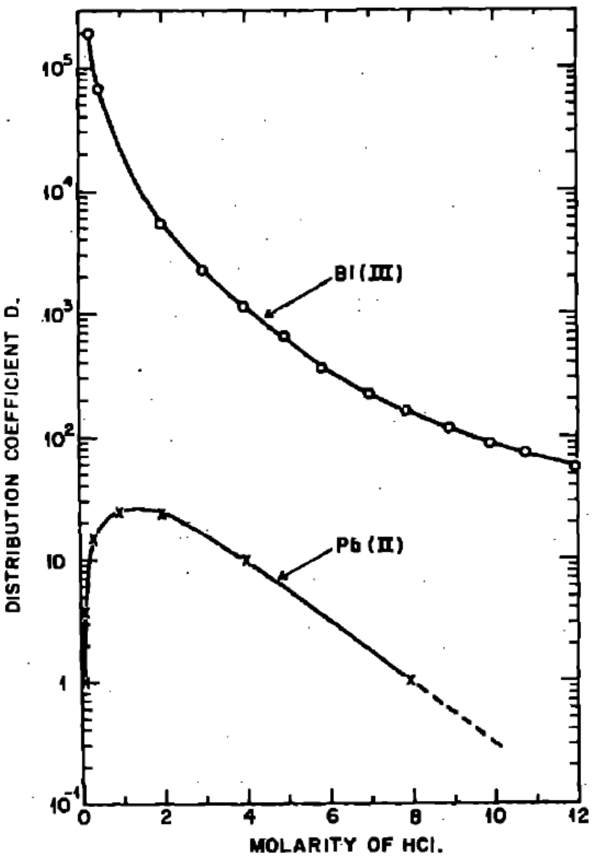
Tab. 30: Method development of the spontaneous deposition

Experiment No.	Deposition time (h)	Disc material	Temp. (°C)	Yield (%)	Matrix composition
1	3	Nickel	50	38	Po-208 tracer (100 mBq) carrier free + 100 mg ascorbic acid
2	3	Nickel	65	47	
3	3	Nickel	85	57	
4	5	Nickel	85	51 (50–52)	Po-208 tracer (100 mBq), 50/50 of HCl/HNO_3 (both $c = 0.5$ mol l^{-1}). No ascorbic acid.
5	5	Nickel	85	61 (57–65)	Like above, but with 100 mg ascorbic acid
6	5	Nickel	85	76 (86–70)	Po-208 tracer (100 mBq) carrier free + 100 mg ascorbic acid
7	5	Stainless steel	85	56	Po-208 tracer (100 mBq) carrier free + 100 mg ascorbic acid
8	5	Silver	85	80	Po-208 tracer (100 mBq) carrier free + 100 mg ascorbic acid
9	18	Silver	85	98	
10	5	Silver	85	41	Pb-210 tracer in equilibrium with Bi-210 and Po-210 (35 mBq) + Pb carrier
11	18	Silver	85	69	

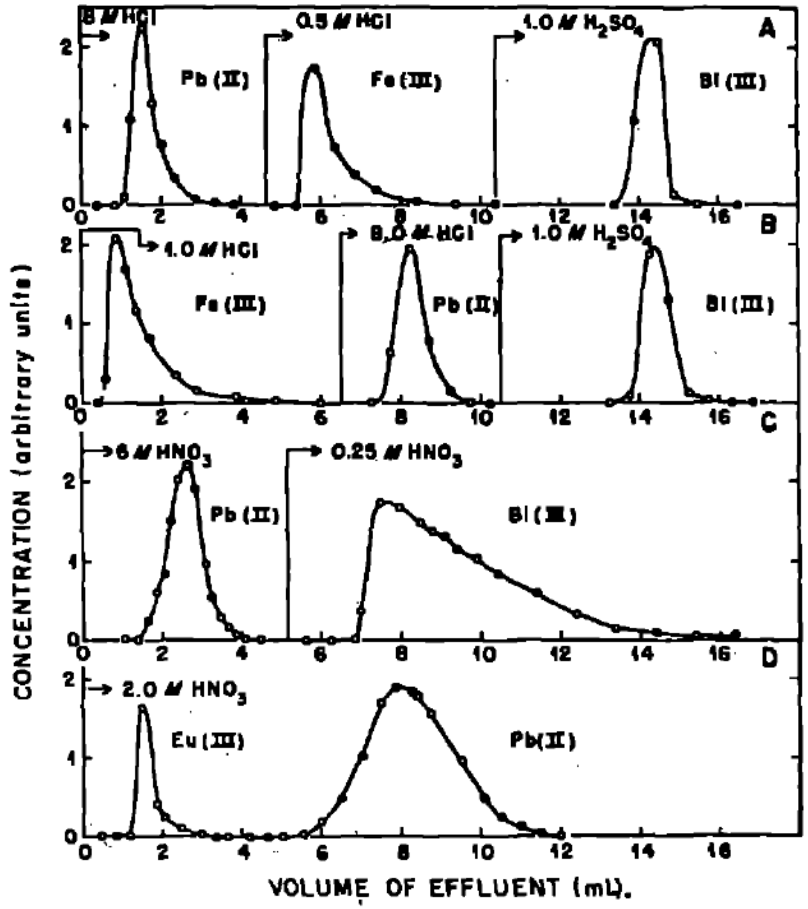
….separation of Pb-Bi-Po



26. Distribution coefficients for adsorption of elements onto Dowex-A-1 anion exchange resin from hydrochloric acid. From K. A. Kraus and F. Nelson, Proc. of the First U.N. Conf. on Peaceful Uses of At. Energy 7, 113 (1955).



Distribution coefficient vs. hydrochloric acid concentration for adsorption of lead and bismuth on Dowex-A-1 anion exchange resin from hydrochloric acid solution. From F. Nelson and K. A. Kraus, J. Am. Chem. Soc. 76, 5916 (1954).



Separations involving PbII in hydrochloric acid and nitric acid solutions (0.30 sq. cm. columns, length A, 4.7 cm; B, 4.7 cm; C, 6.8 cm; D, 12.2 cm, 200-300 mesh Dowex-1, flow rate, 0.5 cm/min). From F. Nelson and K. A. Kraus, J. Am. Chem. Soc. 76, 5916 (1954).

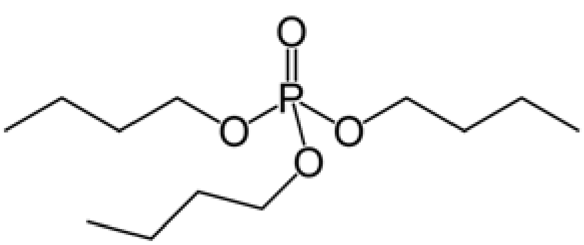
Uranium

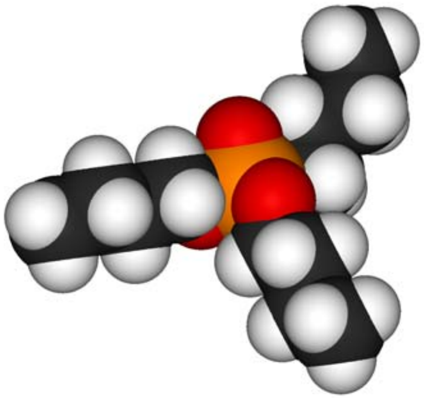
• Matrix elements
• Interferences in alpha spectrometry:
  • U-234 & Th-230
  • U-232 & Po-210

Separation method based on extraction with Tributyl phosphate $PO(OC_4H_9)_3$

Tracer isotope: U-232 (decays to Th-228). Care must be taken in combined analysis of U & Th to clean U-232 tracer from Th-228.

$UO_2(TBP)_2(NO_3)_2$





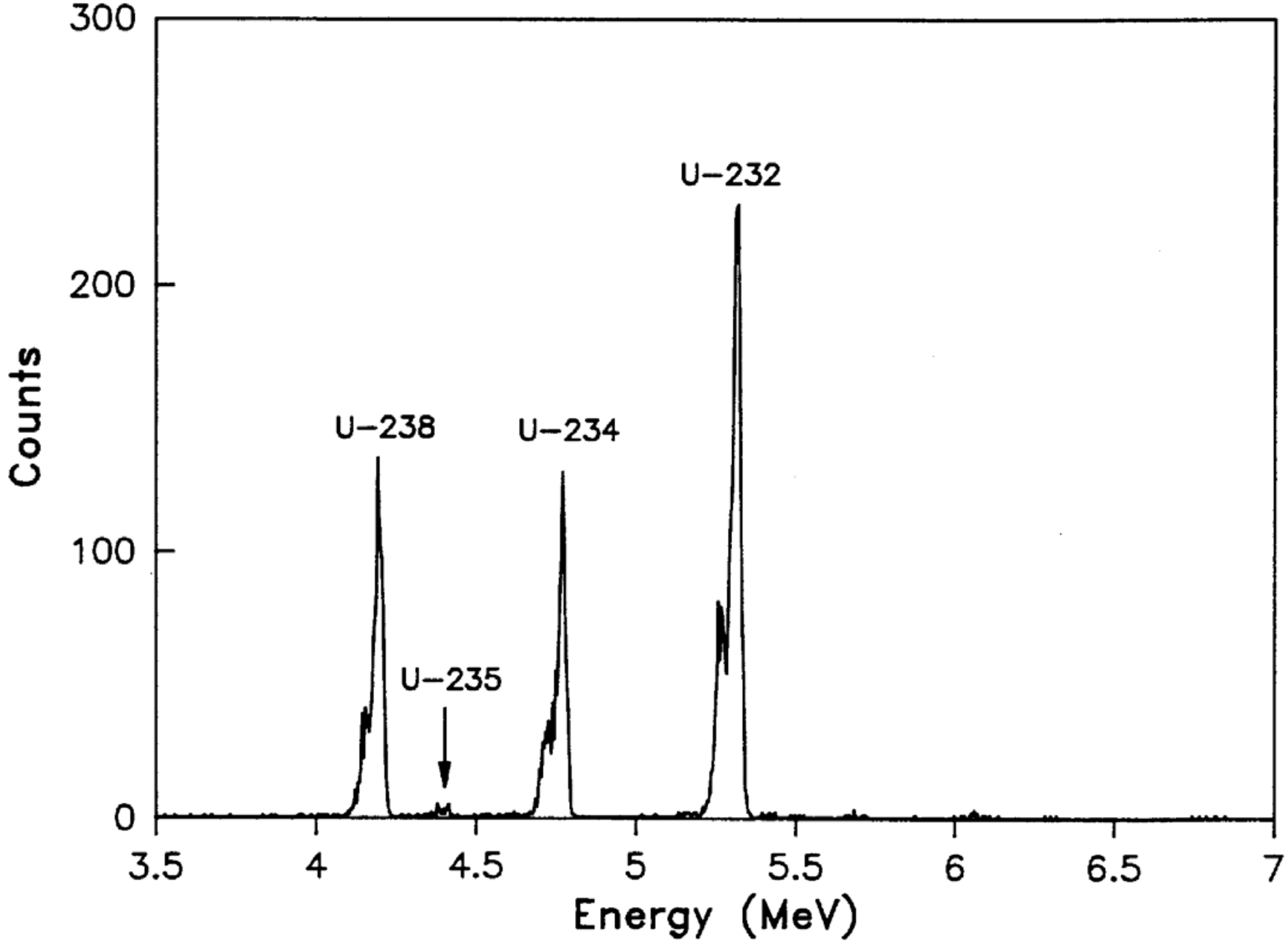


Figure 17. Typical uranium spectrum
Tracer isotope: ^{232}U

Thorium

- Matrix elements
- Interferences in alpha spectrometry:
    - Th-230 & U-234

Separation method based on extraction with Tributyl phosphate $PO(OC_4H_9)_3$ + in some cases a short anion exchange column.

Tracer isotope: Th-229 (large amount interfere with Th-230)

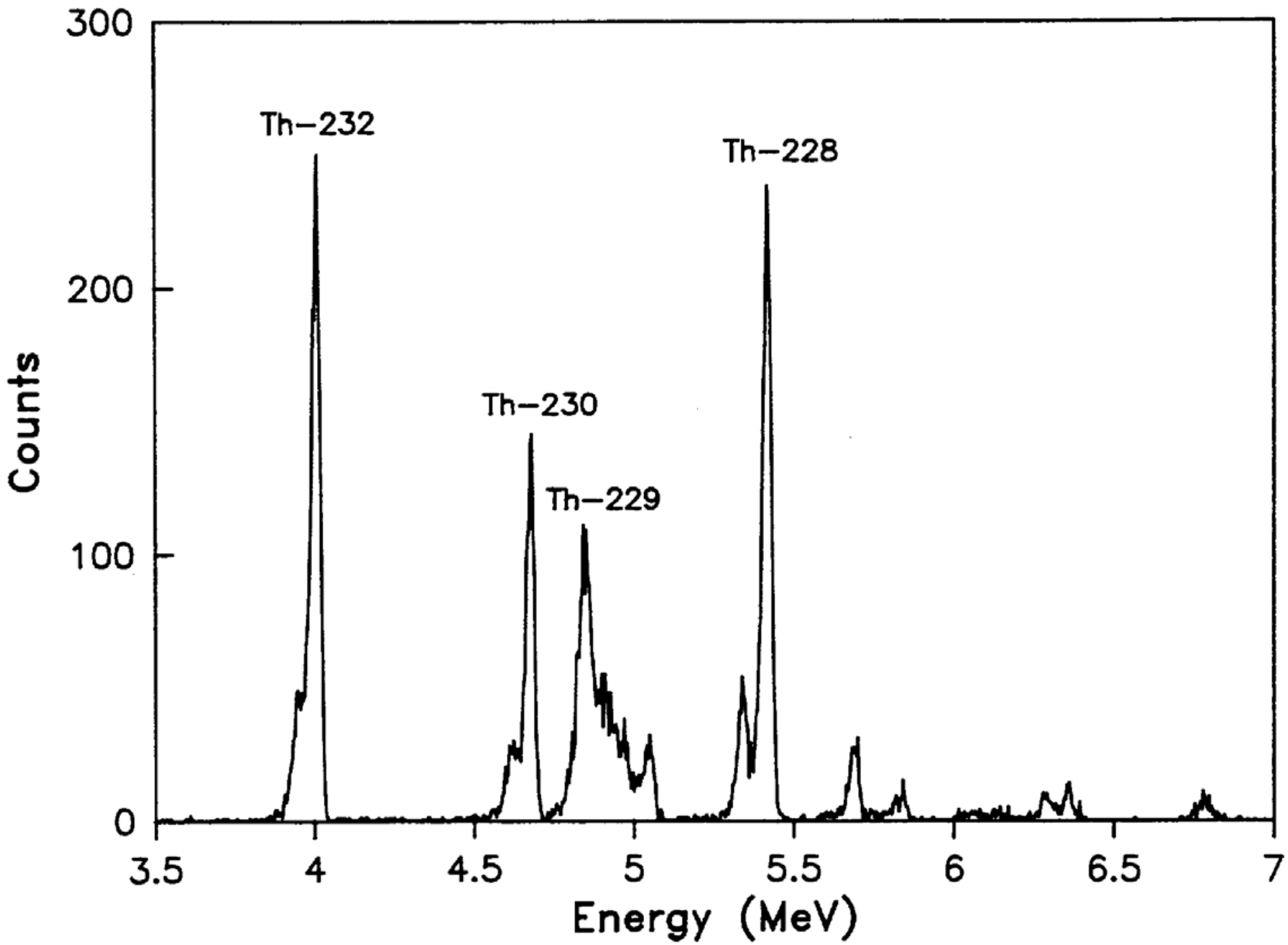
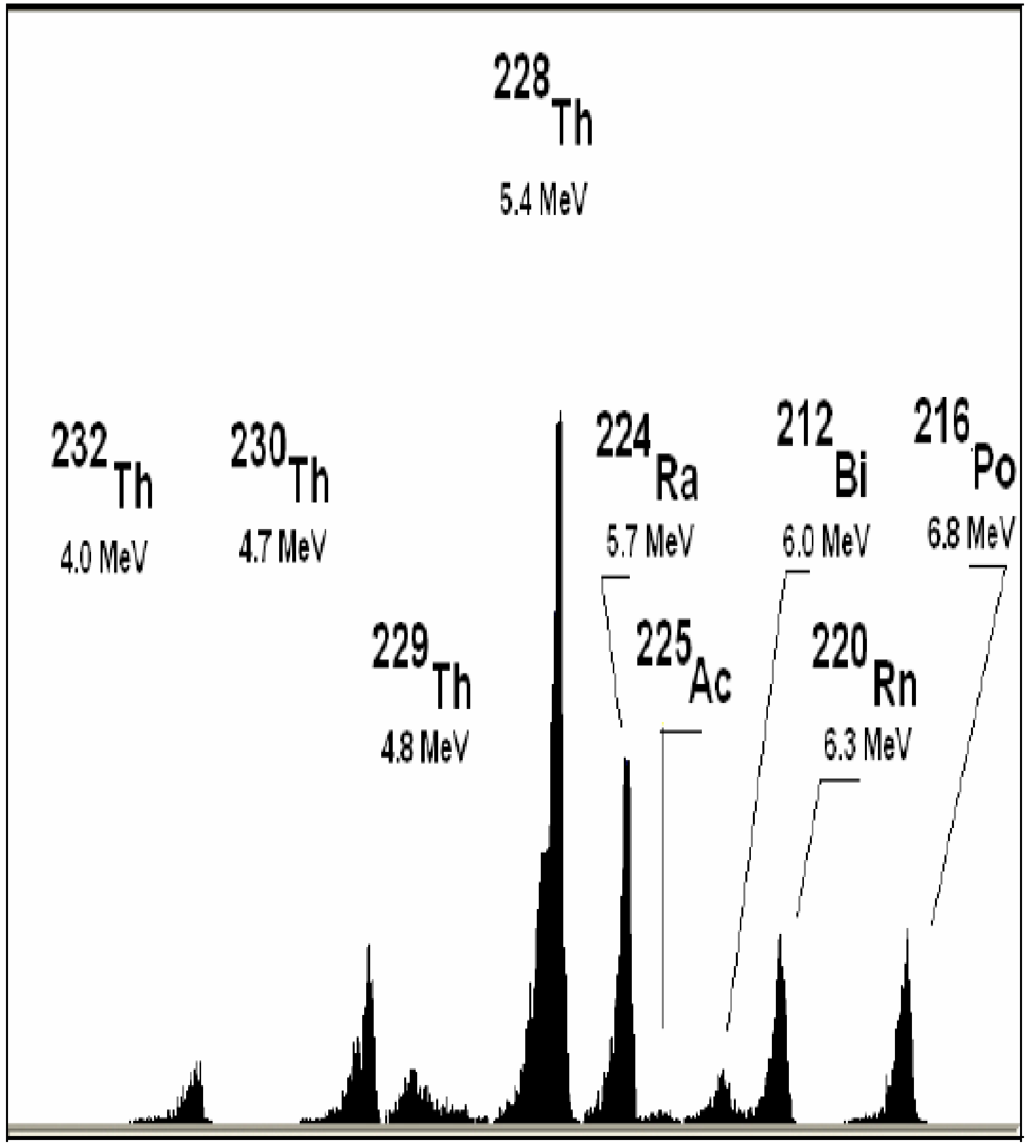
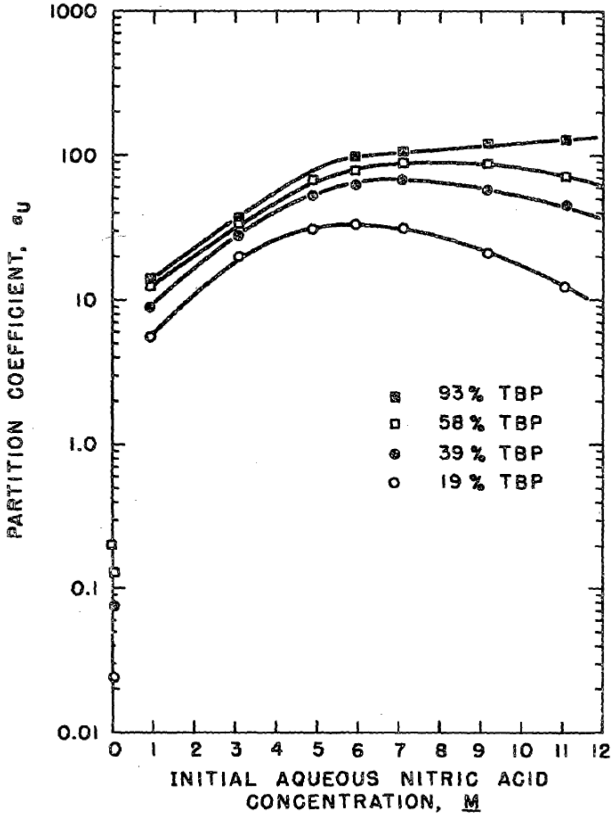


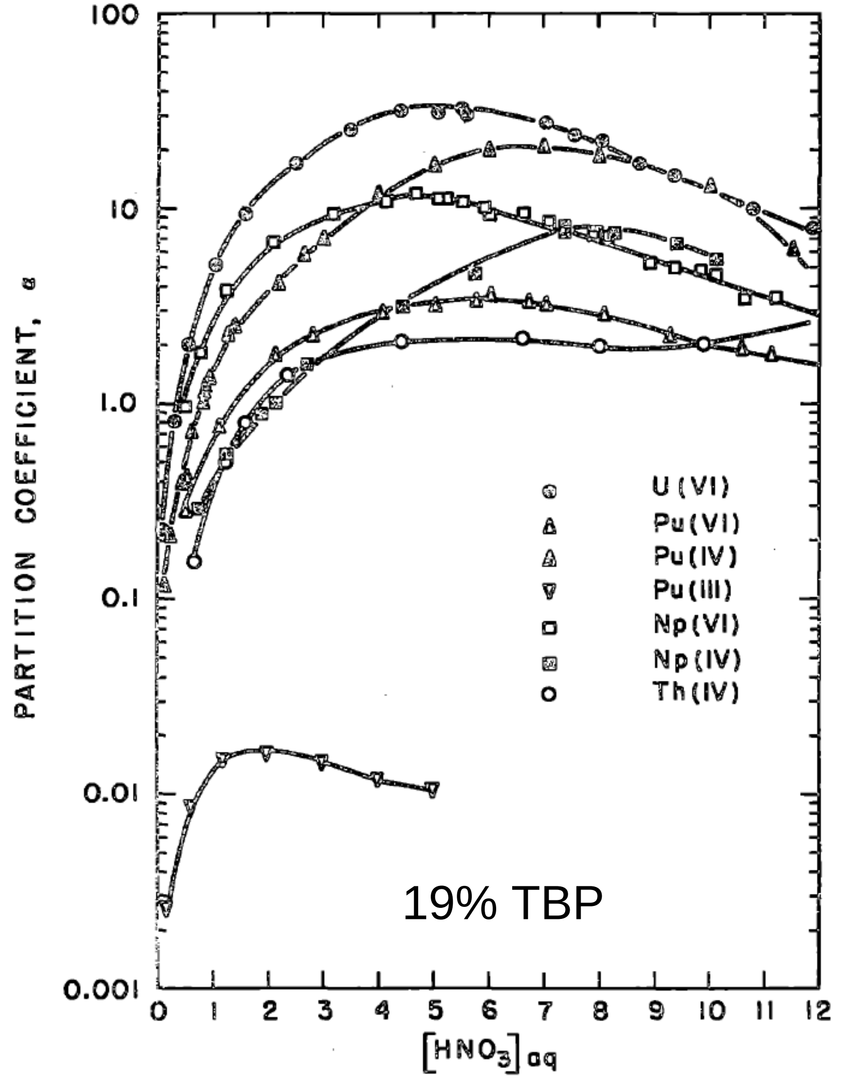
Figure 18. Typical thorium spectrum
Tracer isotope: ^{229}Th



228Th
5.4 MeV
232Th
4.0 MeV
230Th
4.7 MeV
229Th
4.8 MeV
224Ra
5.7 MeV
225Ac
212Bi
6.0 MeV
220Rn
6.3 MeV
216Po
6.8 MeV

U & TBP





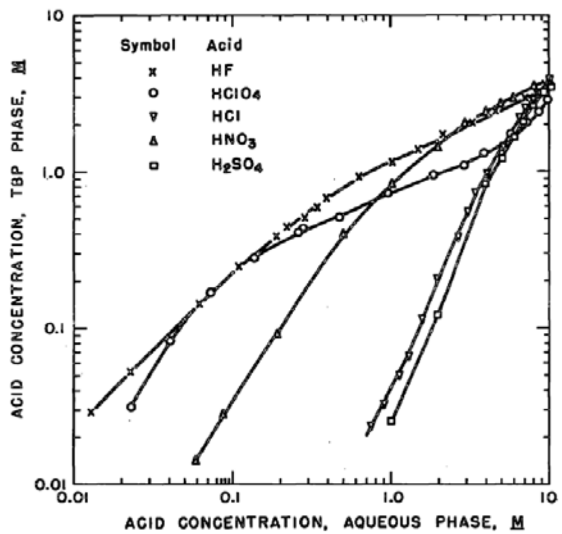


Figure 34.

TABLE 19

EXTRACTION COEFFICIENT DATA FOR TBP[149]

Ion	Solution	TBP (%)	Extraction Coefficient At 25°C
Am(III)	4.0M HNO_3	30	0.013
Al	4.7M	15	0.0003
Ca	4.7M	15	0.0003
Co(II)	2.14M $Co(NO_3)_2$	60	0.002
Cr(III)	3.0M HNO_3	100	0.0001
Cu(II)	3.0M	100	0.0004
Fe(II)	4.7M	15	0.005
Fe(III)	2.0M	12.5	0.003
Mg	4.7M	15	0.0003
Na	2.0M	12.5	0.003
Ni(II)	3.0M	100	0.00006
Np(IV)	4.0M	30	3.0
Np(VI)	4.0M	30	12.0
Th	4.0M	30	2.8
Pa	4.0M	50	2.8
Zn	2.0M $Zn(NO_3)_2$	12.5	0.0001
Ru	2.0M HNO_3	30	0.15
Zr	2.0M	30	0.09
Nb	2.0M	30	0.03
Rare earths	2.0M	30	0.02
Pu(III)	5.0M	20	0.012
Pu(IV)	5.0M	20	16.6
Pu(VI)	5.0M	20	2.7
U(IV)	4.0M	25	10
U(VI)	4.0M	25	23
HNO_3	2.0M	30	0.26

Th & TBP - HNO_3

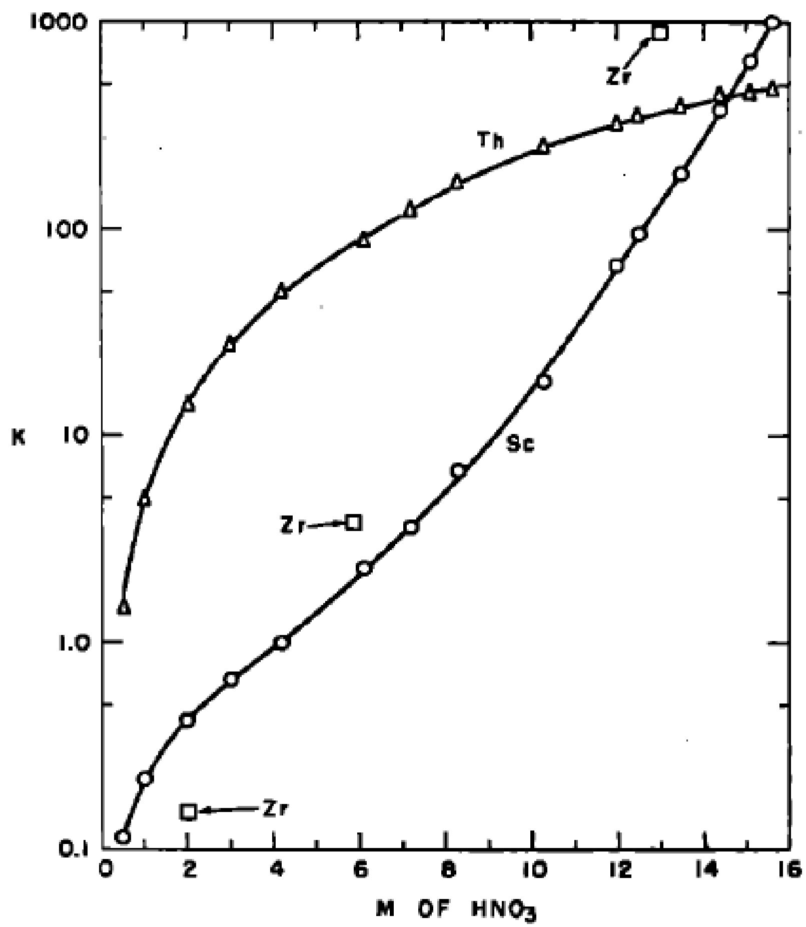


Figure 4 Variation of distribution ratios (TBP/aqueous) of scandium, thorium and zirconium with aqueous HNO_3 concentration for extraction into pure undiluted TBP. Peppard, Mason and Maier[42].

Th & TBP - HCl

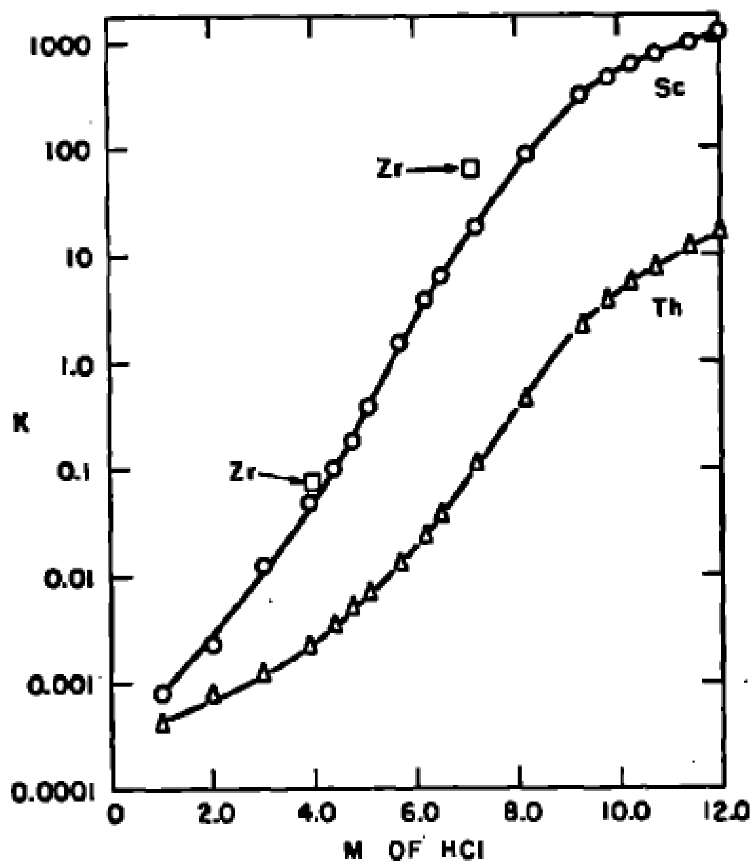


Figure 3 Variation of distribution ratios (TBP/aqueous) of scandium, thorium and zirconium with aqueous HCl concentration for extraction into pure, undiluted TBP. Peppard, Mason and Maier[42].

Salting out agents

TABLE 6 EFFECT OF CONCENTRATION OF $Ca(NO_3)_2$ IN THE AQUEOUS PHASE ON THE EXTRACTION OF THORIUM INTO UNDILUTED TBP. (Bernström and Rydberg[41])

$Ca(NO_3)_2$ Conc	HNO_3 Conc	K_{th}(TBP/Aq)
0	1-4 M	4-20
1 M	1-4 M	60-200
2 M	1-4 M	310-550
3 M	1-4 M	1400

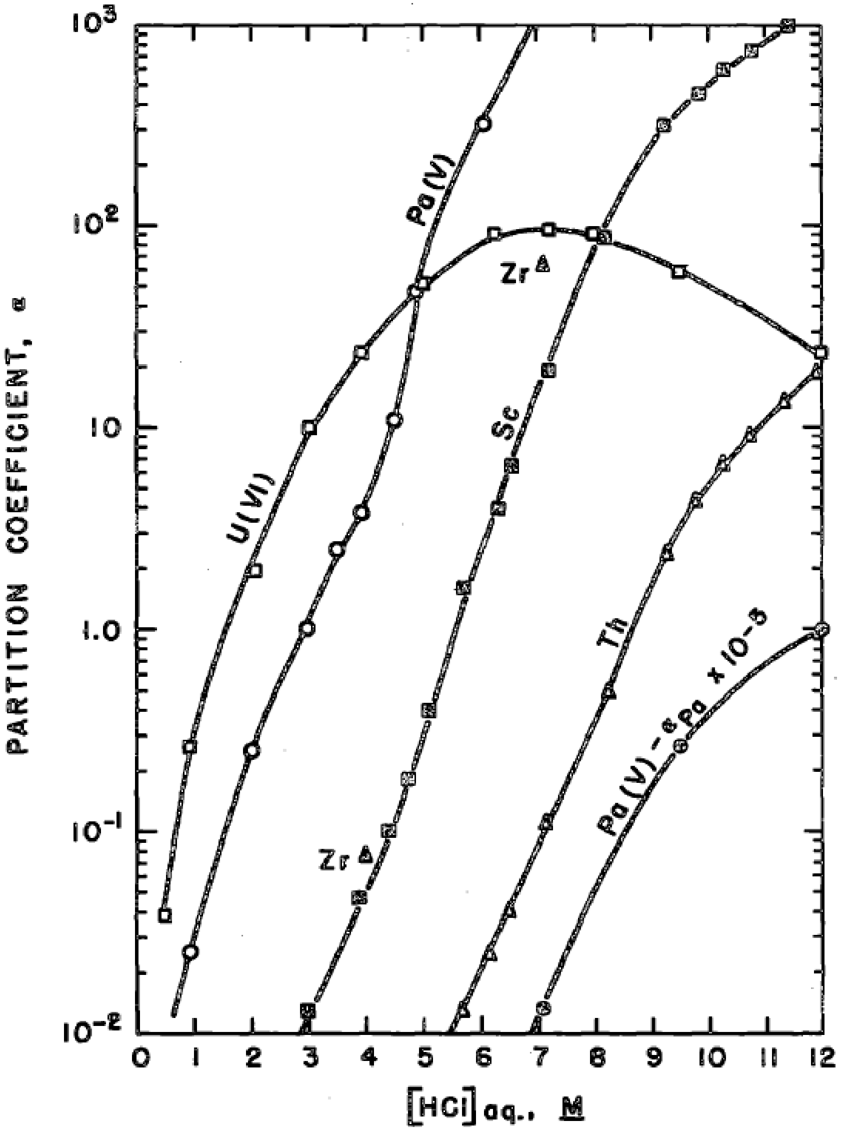


Figure 38. The extraction coefficient of U, Pa, Th, Zr, and Sc between pre-equilibrated 100% TBP and aqueous hydrochloric acid at 22° ± 2°C. After D. F. Peppard, G. W. Mason, and M. V. Gergel, reference 429, and D. F. Peppard, G. W. Mason, and J. L. Maier, reference 422.

U-Th radiochemistry

Remove major elememts (Fe,Al, Ca etc.)

Remove alpha emitting interferences:

Uranium (^{210}Po, Th-isotopes)
Thorium(Uranium isotopes, ^{210}Po)

- Extract U & Th from 20ml 8M HNO_3 in 5ml TBP (Tri-n-Butyl-Phosphate).
- Wash with 2-3 times 20 ml 8M HNO_3.
- Add 15ml Xylene to the TBP
- Back-extract Th using 2*20ml 1.5M HCl
- Back-extract U using 2*20ml H_2O
- Electrodeposit